Vapor Pressure of Aluminum Chloride Systems. 3. Vapor Pressure of Aluminum Chloride–Sodium Chloride Melts

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The vapor pressures of liquid aluminum chloride–sodium chloride mixtures containing 53–74 mol % aluminum chloride were measured from the condensation temperatures of solid aluminum chloride to 251 °C. Samples were contained in Pyrex isoteniscopes which utilized mercury as the manometric fluid. The mercury columns were brought to null by an external pressure which was in turn measured at each experimental point. The experimental pressures were fit to a single equation which serves the entire composition–temperature region.

We measured the vapor pressure of aluminum chloride–sodium chloride molten mixtures as part of our continuing investigation of low-melting molten salt battery electrolytes. Previously reported vapor pressures of this system (*2*, *3*, *5*, *6*) are in disagreement by more than an order of magnitude.

Experimental Section

Preparation of the $AlCl_3$, the glovebox atmosphere, loading of the isoteniscope, the constant temperature bath and its temperature regulation and measurement, and the measurement of vapor pressure were all as described previously (*10*). A mercury manometer was used as an additional external pressure measurement device.

Powdered mixtures of $AlCl_3$ and NaCl were loaded into a Pyrex isoteniscope similar to that used for saturated $AlCl_3$ vapor pressures (*10*). NaCl was dried by maintaining it molten for several hours (*7*). The $AlCl_3$–NaCl mixtures were prepared by grinding and mixing weighed amounts of $AlCl_3$ crystals with weighed amounts of dry NaCl crystals in a glovebox.

Results

A total of 227 measurements on 12 different compositions were taken at values of mole fraction and temperature that lay within a polygon on the X,t plane described approximately by the coordinates (X, t) = (0.54, 149), (0.58, 106), (0.61, 103), (0.70, 175), (0.74, 182), (0.74, 251), and (0.54, 251). Pressure measurements were made at both ascending and descending temperature steps, and equilibrium was assured at each point by maintaining constant temperature for many minutes until pressure remained constant within measurement error. The samples were stirred by vigorous shaking before each measurement to prevent the formation of internal concentration gradients.

The data are given in Table I. Pressures have been corrected for the vapor pressure of mercury within the isoteniscope. Interactions between Al_2Cl_6 vapor and Hg vapor were assumed to be negligible. The measurement method for each datum is indicated in the table. Several additional measurements were made at temperatures lying below the X,t polygon for each of the eight compositions richest in $AlCl_3$. These pressures lay on the curve of saturated vapor pressure of solid $AlCl_3$ (*10*), and fell distinctly away from the X,p,T surface for $AlCl_3$–NaCl melts.

We assumed the vapor pressure of $AlCl_3$–NaCl melts could be represented by an equation of the form

$$\log p = (A/T) + B \qquad (1)$$

where

$$A = A_0 + A_1X + A_2X^2$$
$$B = B_0 + B_1X + B_2X^2 \qquad (2)$$

The vapor pressures of individual compositions were fit by other investigators to equations of the form of eq 1 (*3*, *5*, *6*) or eq 1 modified by the addition to the right-hand side of the term $\Delta C_p/R \log T$ (*1*, *2*).

The data were least-squares fit in such a way as to minimize the perpendicular distance, z, from the experimental points to the function surface in X, p, and T given by eq 1 and 2. This procedure is similar to the fitting technique used earlier (*10*). The equations were solved for the values of A_j and B_j which minimized the sum, $\sum_{i=1}^{N} z_i^2$ where

$$z_i = \left[\left(\frac{\delta p_i}{\Delta p_i}\right)^2 + \left(\frac{\delta T}{\Delta T_i}\right)^2\right]^{-1/2} \qquad (3)$$

In eq 3, δp_i = the greater of 0.1 Torr or 0.005 p, δT = 1 K, $\Delta p_i = p_{\exp,i} - \exp[(A_i/T_{\exp,i} + B_i)\ln(10)]$, and $\Delta T_i = T_{\exp,i} - A_i/(\log p_{\exp,i} - B_i)$. As indicated in eq 2, A and B are functions of X. Since there was an appreciable vapor space in the isoteniscope (ca. 85 cm^3), the true mole fraction, x, of the melt will be different for each experimental point, depending upon the nominal mole fraction, X, and upon temperature. Accordingly, for every experimental point

$$A_i = A_0 + A_1x_i + A_2x_i^2$$
$$B_i = B_0 + B_1x_i + B_2x_i^2 \qquad (4)$$

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Table I. Experimental Data

t, °C	p,[a] Torr	t, °C	p,[a] Torr	t, °C	p,[a] Torr	t, °C	p,[a] Torr	t, °C	p,[a] Torr	t, °C	p,[a] Torr
X = 0.537 90		242.26	31.35 H	188.25	33.99	226.27	188.68	196.37	159.86 H	230.96	674.34
158.28	3.67 M	242.26	33.14	189.66	34.93 H	231.94	205 07	196.37	162.39	249.68	914.98
158.28	4.33 H	250.59	30.99 H	189.66	35.53	237.23	224.53	204.16	209.38 H	250.95	931.64
190.33	8.52 M	250.59	32.70	222.84	79.45 H	242.75	238.63	204.16	211.83		
190.33	7.97			222.84	81.05	250.90	265.59	206.99	186.25 H	X = 0.692 77	
217.83	12.79 H	X = 0.5 5 13		244.87	109.91 H			206.99	191.41	166.19	322.59
217.83	12.13	142.21	2.64 M	244.87	113.38	X = 0.626 77		209.63	201.75 H	171.93	380.53
		142 21	4.03 H	247.65	115.87 H	137.00	21.14 H	209.63	208.17	176.47	422.99
X = 0.542 50		142 27	2.86 M	247.65	119.29	137.00	22.04 M	210.01	202.17 H	183.69	506.47
144.79	3.23 H	142 27	3.90 H	247.67	114.53 H	137.05	21.16	210.01	209.20	190.66	591.83
144.79	3.30 M	152.07	4.68 H	247.67	115.78 H	148.31	32.59 H	224.30	284.72	201.35	735.97
144.79	2.59	152.26	4.86 H	247.67	117.90	148.31	32.50	234.38	343.94	212.22	907.08
155.58	3.16 M	153.06	4.79 M	247.67	119.21	162.05	50.40 H	256.55	506.30	221.97	1076.42
155.58	3.13 H	153.06	4.96 H	247.70	113.53 P	162.05	51.04			231.04	1255.05
155.58	3.29	163.70	6.41 M	247.70	116.64	166.53	54.35 H	X = 0.659 04		237.21	1385.44
155.87	4.42 M	163.70	6.43 H			166.53	56.70	155.61	114.77 H	250.21	1675.66
155.87	4.38 H	169.21	6.50 H	X = 0.609 77		173.06	71.21 H	155.61	117.53		
155.87	3.37	169.21	7.11 M	134.86	12.39 M	173.06	72.61	177.72	199.88 H	X = 0.702 55	
182.34	6.00 M	179.69	8.86 H	134.86	12.84	185.66	98.60 H	177.72	205.24	174.67	470.55
182.34	6.62 H	179.69	9.14 M	139.73	14.54 M	185.66	98.53	193.58	295.20	183.22	573.93
182.34	7.32 H	186.49	10.64 H	139.73	14.81	198.48	136.68 H	209.87	395.03	192.82	698.04
182.34	7.80 M	186 49	11.34 M	144.91	17.70 H	198.48	140.69	212.21	408.33	201.36	835.45
182.34	6.26	194.50	13.14 H	144.91	18.19 M	210.15	175.69 H	225.92	533.74	209.66	976.29
182.34	7.72	202.75	16.04 H	144.91	18.70	210.15	185.43	226.22	508.17	X = 0.739 29	
190.41	10.28 H	X = 0.580 62		150.12	21.64 H	224.48	247.37	226.33	529.68	182.02	934.82
190.41	10.68 M	105.67	2.26 M	150.12	22.75 M	236.39	305.04	240.06	569.23	189.20	1122.00
190.41	9.65	105.67	2.11	150.12	22.78	250.89	396.51	242.59	675.56	190.31	1146.63
195.93	9.81 H	127.55	5.10 M	155.74	26.00 H			250.84	799.90	197.83	1336.35
195.93	10.97 M	127.55	4.74	155.74	27.56	X = 0.630 46		250.98	800.52	204.09	1524.16
195.93	9.94	128.95	5.13 M	163.35	33.40 H	134.17	26.76 H			211.59	1748.73
199.10	12.01 H	128.95	5.03	171.69	44.26 H	134.17	26.75	X = 0.660 36		225.99	2254.49
199.10	12.12	150.05	9.40 H	179.55	55.89 H	151.03	44.83 H	153.55	102.90 H	226.61	2294.22
209.33	14.86 H	150.05	9.56 M	187.95	71.90 H	151.03	45.38	153.55	104.10	230.85	2478.87
209.33	15.12	160 07	13.98 M	196.40	90.26 H	152.39	44.11 H	157.88	118.12 H	239.46	2825.83
220.61	20.53 H	160.07	14.30 H	204.32	110.78 H	152.39	47.74	157.88	118.89	239.54	2846.17
220.61	20.68	160.07	14.17	212.49	134.75 H	166.95	72.58 H	174.16	187.30 H	239.62	2829.08
225.85	21.63 H	183.10	28.87 H	212.49	137.08	166.95	74.44	174.16	192.13	245.17	3089.51
225.85	22.42	183.10	28.54	220.72	163.42 H	179.71	97.30 H	180.13	229.65	246.00	3113.01
237.59	25.93 H	188.25	33.91 H	220.72	167.36	179.71	98.86	195.82	341.97	250.89	3353.37
237.59	27.09			226.27	182.89 H	182.58	108.14 H	204.20	401.04	251.03	3358.08
						182.58	109.87	222.71	583.06		

[a] The symbols "H" and "M" indicate the use of a mercury manometer and a McLeod gauge, respectively, for pressure measurement; all other pressure measurements were made with a capacitance manometer.

The van der Waals equation obtained previously (*9*) was solved for the number of moles of Al_2Cl_6 in the vapor phase at each experimental point, and the nominal mole fractions were corrected to obtain x_i. The equation is cubic in the number of vapor-phase moles and was solved by the Newton–Raphson technique. The solution was iterated until x_i did not change more than one part in 1000. (Actually, only a single application of the Newton–Raphson technique was necessary for all points except the ten highest temperature data of the sample for which $X = 0.73929$.) Mole fraction corrections ranged from −0 000 01 to −0.009. Many of the corrections were very small but were included because all were in the same direction.

The least-squares fit was iterative. After each iteration any points for which $z \geq 3\sigma$ were eliminated and the remaining data were fit in the next iteration. The standard deviation, σ, was calculated from

$$\sigma = [(1/N)\sum_{i=1}^{N} z_i^2]^{1/2}$$

Iterations were continued until

$$\frac{2|(\sigma - \sigma_{\text{previous iteration}})|}{\sigma + \sigma_{\text{previous iteration}}} \leq 1.0 \times 10^{-7} \qquad (5)$$

The values of A_j and B_j for eq 1 and 2 which are given in Table II are those obtained when the criterion of eq 5 was first satisfied. Seven of the original 227 points were more than 3σ away from the calculated X,p,T surface. These do not appear in Table I. The root mean square value of the quantity |z − true perpendicular|/(true perpendicular) was 0.008. The root mean square percentage errors in pressure and temperature for all points were 2.5 and 0.65%, respectively. The surface generated by eq 1 and 2 is shown in Figure 1.

Table II. Least-Squares Fit Parameters for Equations 1 and 2

$A_0 = 6064.90$	$s_p = 1.4$ Torr
$A_1 = -29406.3$	$s'_p = 2.5\%$
$A_2 = 25360.7$	$s_T = 3.1$ K
$B_0 = -26.2772$	$s'_T = 0.65\%$
$B_1 = 100.6062$	
$B_2 = -75.1432$	

In addition to the 12 samples described above, two more $AlCl_3$–NaCl melts were examined, for which the nominal mole fractions were 0.896 and 0.925. We noted the same separation into two phases which Kendall et al. (*4*) reported for $X > 0.82$. The pressures of these two samples were the same as the pressures of saturated liquid $AlCl_3$ (*10*) at the same temperatures over the temperature range 184–238 °C, with a root mean square pressure difference of 1.5%.

Discussion

Remarkable discrepancies among reported $AlCl_3$–NaCl melt vapor pressures exist in the literature. Naryshkin (*6*) reported vapor pressures smaller than are reported in the present work at the same temperatures and compositions by factors ranging from 2 to 17. Galitskii's vapor pressures (*3*) are as much as

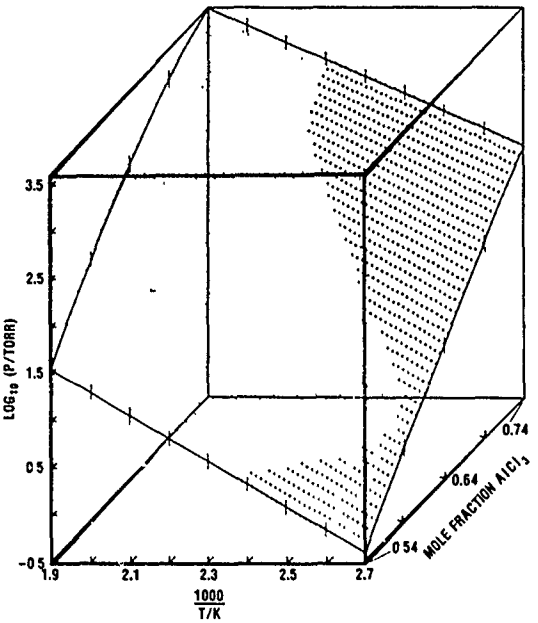

Figure 1. X, log p, $1/T$ surface for vapor pressure over $AlCl_3$–NaCl liquid mixtures. Points are calculated from eq 1 and 2: ·, density within X, t range experimentally covered; +, extrapolated values. For clarity, surface is extrapolated to intersect faces of cube.

70-fold smaller! Dewing (*2*) studied four compositions in the range $X = 0.54$–0.66. His apparatus utilized an internal manometer wherein the $AlCl_3$–NaCl melt itself was the manometric fluid. His results are depicted graphically only, but Davey et al. (*1*) calculated vapor pressure equations of the form

$$\log p = \Delta C_p/R \log T + A/T + B$$

from Dewing's results. These values agree reasonably well with the present work; the differences range from −1 to −4% for one composition and from 12 to −21% overall. Davey et al. (*1*) also gave the unpublished results of Rogers (*8*), who investigated five compositions in the composition range $X = 0.53$–0.69. Rogers' pressures match both those obtained in this study and Dewing's but show more scatter and yield both higher and lower pressures than either of the two other studies.

The most complete study previously reported, both in numbers of samples, 7, and in composition range, $X = 0.54$–0.75, is that of Narita et al. (*5*). They used an isoteniscope with mercury as the manometric fluid. Their results are lower than those of Dewing (*2*), Rogers (*8*), and the present work by a factor of 2–5.

No readily obvious reason has been suggested for the great discrepancies noted among the several studies reported. However, $AlCl_3$-containing melts are notoriously difficult to obtain and keep free from contamination, and most likely contaminants would reduce the vapor pressure. An exception to this is the presence of dissolved gases. Both Dewing (*2*) and Narita et al (*5*) have commented on the presence of a residual gas pressure once a melt had been heated to well above its melting point then cooled to some lower temperature. Narita et al. were able to pump out the residual gas. Dewing corrected for its presence by assuming the residual gas partial pressure was governed by the ideal gas law. We pumped out the residual gas, but first froze the sample and cooled it to room temperature to avoid removing any $AlCl_3$ at the same time. Initial residual pressures varied from a few Torr to around 100 Torr. We would repeatedly remelt and refreeze each sample until the residual pressure was undetectably small. The residual gas from two samples was analyzed mass spectrometrically. One sample was essentially all HCl and the other contained in addition a small amount of N_2

The volatility correction referred to earlier was not mentioned by the other investigators. The correction may be rather substantial at high T and X. For example, the vapor pressure of the last point in Table I is 12% lower than the calculated vapor pressure of a sample whose composition is actually at the nominal value, $X = 0.739\,29$. It is not possible to tell from the information furnished whether volatilization errors were large in the previously published studies, or even if they contributed to the much smaller pressures observed by Galitskii (*3*), Narita et al. (*5*), and Naryshkin (*6*).

The study presented here is the most extensive reported on this system, both in regard to the number of measurements made in the temperature–composition range investigated and in the numerical evaluation. A detailed thermodynamic analysis of the data presented in this paper will be made in a forthcoming publication in conjunction with another study on the $AlCl_3$–NaCl system.

Glossary

A	fitted constant
B	fitted constant
C_p	heat capacity at constant pressure, cal mol^{-1} K^{-1}
i	index
j	index
ln	natural logarithm
log	logarithm to the base 10
N	the total number of experimental points used in fitting
p	pressure, Torr
R	gas constant, 1.987 cal mol^{-1} K^{-1}
s_p	root mean square of the differences between experimental pressure and pressure at the corresponding intersection of the perpendicular to the chord, Torr
s'_p	root mean square of 100 × the difference between experimental pressure and pressure at the corresponding intersection of the perpendicular to the chord, divided by experimental pressure, %
s_T	root mean square of the differences between experimental temperature and temperature at the corresponding intersection of the perpendicular to the chord, K
s'_T	root mean square of 100 × the difference between experimental temperature and temperature at the corresponding intersection of the perpendicular to the chord, divided by experimental temperature, %
t	temperature, °C
T	temperature, K
x	apparent mole fraction of $AlCl_3$ on $AlCl_3$–NaCl scale after volatility correction
x_0	nominal apparent mole fraction of $AlCl_3$ on $AlCl_3$–NaCl scale
z	perpendicular distance to chord along equation; function to be treated by least-squares fitting
δp	the greater of 0.1 Torr or 0.5% p; estimated uncertainty in pressure measurement
δT	1 K; estimated uncertainty in temperatures of sample
σ	standard deviation

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